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SUPPLEMENTARY INFORMATION

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Materials and pathways of the organic carbon cycle through time

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Supplementary Material

Supplementary Method (main text, Figure 2)

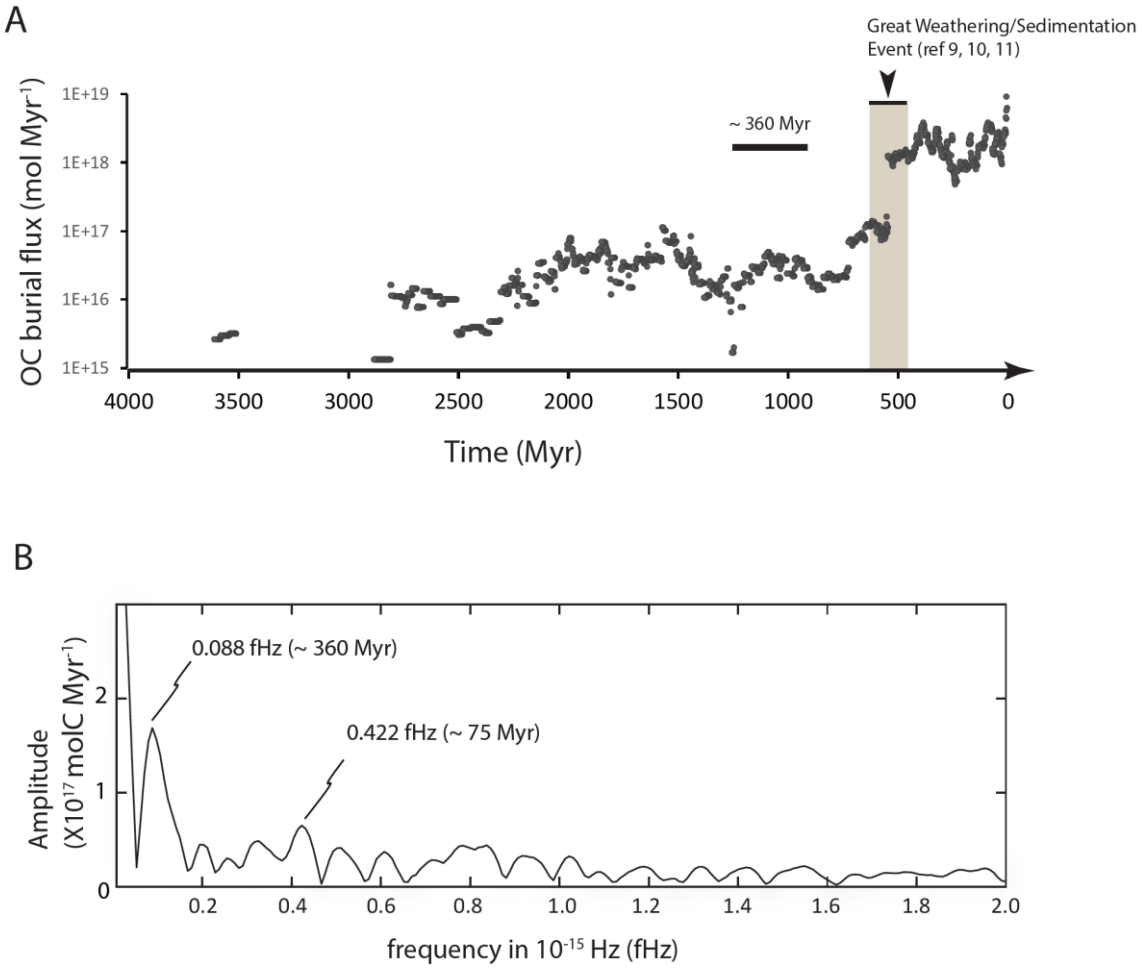
Method: To build ***Fig. 2A***, Thermal data (mass loss) are obtained with a thermogravimeter (Mettler Toledo TGA/SDTA851e) linked with a Balzers ThermoStar Mass Spectrometer (ETH Zurich). We have used a heating ramp of 10 °C per minute from 25 to 1000 °C, and a flow rate of air of 50 mL min^{-1} (Fig. 2). The mass loss data is dominated by reduced carbon for all samples, with minimal contribution from reduced sulfur, and water. Therefore, mass loss is used to derive quantitative information about average oxidation kinetics of C, expressed in the kinetograms of Figure 2. Data inversion uses a non-isothermal first-order decay kinetics [1,2] (Arrhenius formalism) and an Arrhenius pre-factor A = 10^{10} assumed to be time and temperature independent [1]. For sake of simplicity, the regularization parameter (λ) is set to λ = 0.4 to ensure straightforward intersample comparision.

Sample details: Sample 1 is a black shale (peak temperature < 90°C) from the Monte San Giorgio area, Switzerland[3] (Sampling August 2019). Sample 2 is a black shale from the Arramachai formation (peak temperature < 90 °C), Peru (low grade). Sample 3 is a metamorphic calcschist (peak metamorphic temperature of ca. 550 °C) from the East Assietta[4] (schistes lustrées), Italian Alps (sampling May 2019). Sample 4 is a metamorphic carbonate-free carbonaceous schist from Alpine Corsica[5]. Sample 5 is a graphite vein (hydrothermal) from New Hampshire (Franklin Pierce), USA[6]. Sample 6 is from the hydrothermal graphite deposit from Ceylon[7]. Sample 7 is a suspended sediment material from the Marsyandgi river (Himalaya, Nepal, courtesy Lena Märki).

Because the size of graphitic crystallites affect their thermal behaviors[8], all samples were finely powdered to <50 μg in agate mortar before analysis. For vein graphite (sample 4, 5, 6) composed a large crystallites with few silicate materials, the samples were first mixed with pure quartz to ensure homogeneous size distribution within and between samples. Most of the carbon is in reduced form for samples 1,2, 4, 5, 6, so no further extraction procedures (acid) have been applied, and we thermally analyzed about 10 mg of it. Only sample 4 contains carbonates and has been pre-washed with 6M HCl for 6 hours, and then rinced with DI water until neutral pH is achieved.

In ***Fig. 2B***, TEM images (nanotextures of OC_{petro} from samples 1 and 6) were acquired on a Thermofischer Scientific Talos F200X instrument operated 110 at 200kV acceleration voltage.

Supplementary Figure 1



A. Global flux of organic carbon burial (mol/Myr) through time from ref [9]. Indicated are the 'Great Weathering/Sedimentation Event'[10,11] at the transition between the Proterozoic and Phanerozoic eons.

B. Fast Fourier Transform spectrum of the OC burial flux by ref [9]. The horizontal axis is in unit of femtoHerz (10^{-15} Hz). The mode at ca. 0.088 fHz (period of 360 Myr) point to fluctuations in OC burial driven by continental fragmentation and assemblies and their effect on relief distribution, erosion and weathering patterns.

1 Hemingway, J. D., Rothman, D. H., Rosengard, S. Z. & Galy, V. V. An inverse method to relate organic carbon reactivity to isotope composition from serial oxidation. *Biogeosciences* **14**, 5099 (2017).

2 Boudreau, B. P. & Ruddick, B. R. On a reactive continuum representation of organic matter diagenesis. *American Journal of Science* **291**, 507-538 (1991).

3 Bernasconi, S. & Riva, A. in *Generation, Accumulation and Production of Europe's Hydrocarbons III* 179-190 (Springer, 1993).

4 Beyssac, O., Goffé, B., Chopin, C. & Rouzaud, J.-N. Raman spectra of carbonaceous material in metasediments: a new geothermometer. *Journal of Metamorphic Geology* **20**, 859-871 (2002).
5 Galvez, M. E. *et al.* Graphite formation by carbonate reduction during subduction. *Nature Geoscience* **6**, 473-477 (2013).
6 Rumble, D., III, Duke, E. F. & Hoering, T. L. Hydrothermal graphite in New Hampshire: Evidence of carbon mobility during regional metamorphism. *Geology* **14**, 452-455 (1986).
7 Dissanayake, C. B. The origin of graphite of Sri Lanka. *Organic Geochemistry* **3**, 1-7.
8 Jiang, W., Nadeau, G., Zaghib, K. & Kinoshita, K. *Thermal analysis of the oxidation of natural graphite - Effect of particle size*. Vol. 351 (2000).
9 Husson, J. M. & Peters, S. E. Atmospheric oxygenation driven by unsteady growth of the continental sedimentary reservoir. *Earth and Planetary Science Letters* **460**, 68-75 (2017).
10 Galvez, M. E. & Pubellier, M. in *Deep Carbon: Past to Present* (eds Beth N. Orcutt, Isabelle Daniel, & Rajdeep Dasgupta) 276-312 (Cambridge University Press, 2019).
11 Peters, S. E. & Gaines, R. R. Formation of the Great Unconformity as a trigger for the Cambrian explosion. *Nature* **484**, 363-366 (2012).